

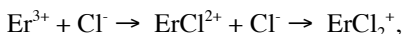
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Determining Free Energies of Metal Complexes in Solution using X-ray Scattering

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Although it is understood that a metal ion dissolved in solution experiences correlations with both solvent molecules and other dissolved ions, quantifying these interactions has been hampered by the absence of an appropriate experimental probe. X-ray absorption fine structure (XAFS) spectroscopy has provided critical information concerning both the presence of correlations and the ions involved, information that has had an impact on modeling metal-ion solubilities, reactivities, and stabilities as a function of solution composition. Unfortunately, technical difficulties with XAFS spectroscopy limit the ability to determine near-neighbor coordination numbers to within an uncertainty of about 10%. This precision is often too low to extract the needed information about the coordination environment. In addition, the second- and higher-neighbor correlations are often inaccessible for study with this technique. We have recently begun to employ high-energy X-ray scattering (HEXS) as a more sensitive probe of metal correlations in solution [1-4]. Our initial experiments have involved dissolved 4f (lanthanide) and 5f (actinide) ions because of their high atomic number and therefore their contrast and overall contribution to the total scattering from aqueous solution. We have been able to extract metrical coordination information for the inner coordination sphere environment within an error of about 2%, and second- and higher-sphere coordination information to about 5%. Changes in metal-ion coordination as a function of anion concentration can now be probed with a precision sufficient to provide the quantitative information needed to determine thermodynamic stability constants for simple metal-ion solution reactions. For example, HEXS provides quantitative structural information on the chloride ion association with Er^{3+} in acidic solution [5],



data that have been used to determine independent stability constants for the inner and outer sphere complexes simultaneously present in solution. Thus the new information provided by the scattering experiments can be used to directly relate the structure of complexes formed in solution with their thermodynamic stability. This capability is providing an entirely new perspective on textbook concepts such as simple inner- vs. outer-sphere complexation and their relative importance to the overall metal energetics. The results are of particular importance to theoreticians who are trying to model solution behavior while explicitly considering only near-neighbor correlations.

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